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Evaluation of spiking methods for the preparation of a Proficiency Testing material in cereal matrices

Measurements of ^{131}I, ^{134}Cs and ^{137}Cs in cereal matrices

Katarzyna Sobiech-Matura
Jean Charoud-Got
Timotheos Altzitzoglou

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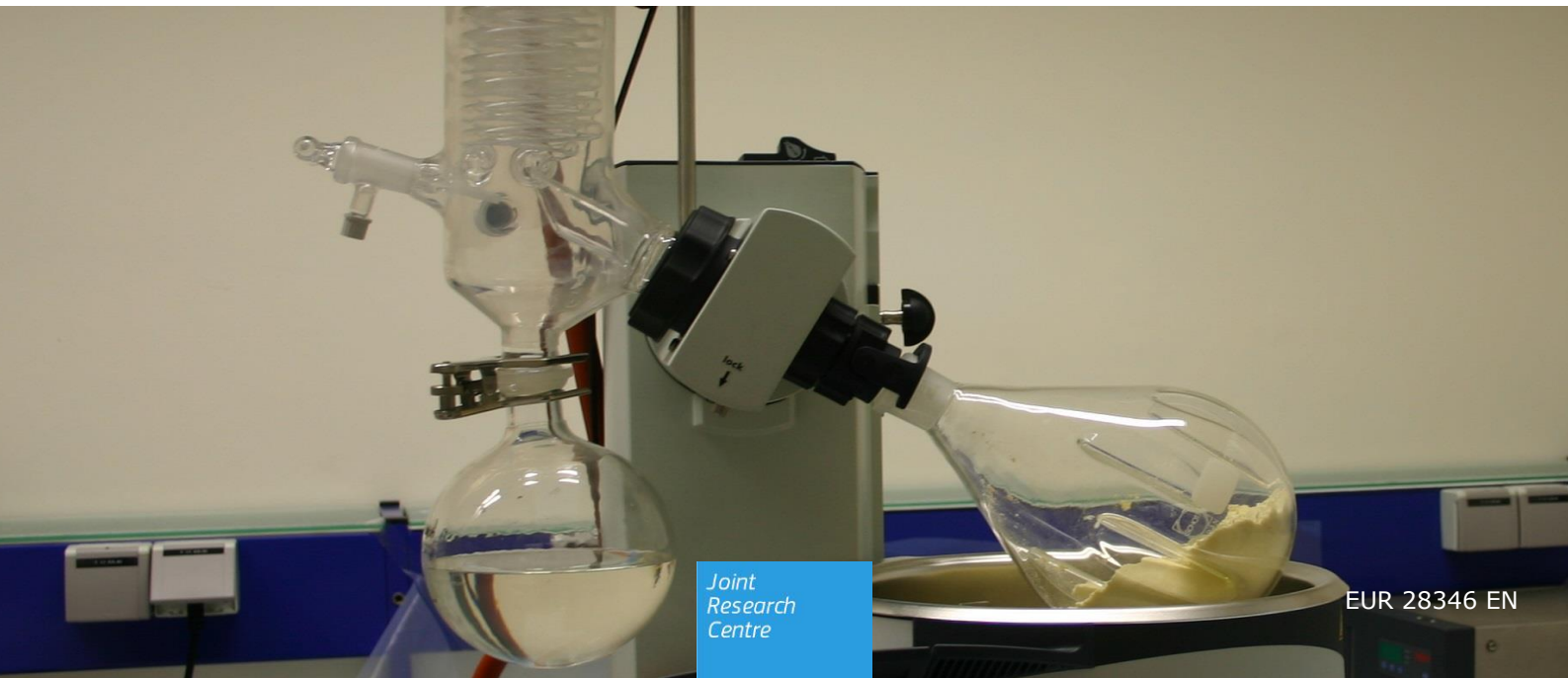

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Contact information
Name: Katarzyna Sobiech-Matura
Address: European Commission, Joint Research Centre, Retieseweg 111, B-2440 Geel, Belgium
Email: katarzyna.sobiech-matura@ec.europa.eu
Tel.: +32 (0)14 571 290

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Contents

Abstract

Among many radionuclides released to the environment during a radiological emergency ^{131}I, ^{134}Cs and ^{137}Cs are usually the most abundant ones. They are transferred to air, water and soil and from those media readily relocated to plants, including those intended for human consumption and for animal feed. Ensuring safe feed is an important component of the efforts to reduce and prevent food safety hazards, especially now, as consumers are increasingly aware of food safety issues and their linkage to animal production, including feeding practices. Therefore it is of utmost importance to ensure that the results of measurements of those three radionuclides delivered by the monitoring laboratories across the EU are reliable in order to guarantee a high degree of feed and food safety. It would be also beneficial to establish a standardised method of analysis for those radionuclides, which requires intra- and interlaboratory tests. In order to conduct such tests a reliable reference material is needed. Since one of the radionuclides (^{131}I) is very short-lived ($T_{1/2}$ = 8.0233 ± 0.0019 days) a spiking method for preparing test samples is necessary. Therefore procedures for spiking of powder were tested. Two methods of material preparation were tested – spiking a bulk sample of powder and individual spiking, where radioactive solution was introduced directly into containers in which samples were being measured. Both methods provided satisfying results. The bulk spiking method was proven to give homogenous samples, which was confirmed by one way analysis of variance (ANOVA) test. In the second method the relative deviation between the amount of the activity added and the calculated activity values was low and lower than the values of uncertainty calculated for the measured activity values. Therefore it can be stated that the closeness of agreement between the activity added to the sample and activity measured was satisfactory. This proves that these samples may be used as a reference material for the method validation and for the next proficiency test planned by the JRC Geel.

1 Introduction

Part of the project 283 – RADMED, in Work package 2260 (CEN Mandate 523 radionuclides in feed) is related to a validation of a measurement method of ^{131}I, ^{134}Cs and ^{137}Cs in animal feed according to the task no. 10 of the CEN Mandate M/523 part III. Those anthropogenic radionuclides are being introduced into the environment as a result of human activities. Their activity concentrations are therefore being monitored in the environment as elevated levels are indications of an emergency situation. During the meeting of Member States' representative for Euratom Treaty Article 35/36 held in JRC Geel on 5-6 April 2016 it was agreed that the next proficiency test will be conducted on maize powder spiked with ^{131}I, ^{134}Cs and ^{137}Cs solutions.

Since one of the radionuclides (^{131}I) is very short-lived (8.0233 ± 0.0019 days half-life) (BIPM-5 Monographie, 2004) spiking of test samples foreseen for method validation or proficiency testing is needed. Therefore the suitability of the spiking procedures of powder was tested. The main objectives were to provide a suitable reference material for method validation and to prove the homogeneity of spiked samples (for the proficiency test samples).

The spiked materials will be used for two different purposes: method validation and proficiency testing. Each purpose has its own requirements, thus needing two different spiking methods. The validation requires assessment of trueness, which is defined as the closeness of agreement between the average value obtained from a large series of test results and an accepted reference value. In order to assess this parameter samples must be spiked directly in the container in which the measurement will be conducted in order to avoid losses of the radioactive solutions, which would have a negative influence on the trueness estimation. For the proficiency testing exercise as well as for the second, interlaboratory phase of the validation, it is required to prepare many homogenous samples. This can be achieved if a method of bulk material spiking is applied followed by homogeneity testing and proper material characterisation.

This report consists of three major parts. First, literature study on spiking procedures and animal feed is presented. Secondly two spiking methods are described and results of their testing are presented. In the last part a conclusion on the results is elaborated.

1.1 Literature study

1.1.1 Spiking procedure

According to the literature there are several methods of spiking samples with known activities of radioactive solutions. The most critical point of a spiking process is to obtain a homogeneous distribution of the radionuclides in the sample.

Spiking was used for the preparation of reference materials already in the 1970s (Sill & Hindman, 1974). There are two main approaches for radionuclide spiking of powders in the preparation of reference materials. The first is to split the bulk starting powder into the final containers and then spike directly each container with the same quantity of radionuclide. The second is to spike the bulk starting powder with an appropriate amount of radionuclide and then distribute it into the separate final containers.

The first approach was used by Shakhashiro et al. (2007) where known aliquot of mixture of gamma-emitting radionuclides was added to methanol directly placed in the containers foreseen for the measurements. It was also used by Shakhashiro and Mabit (2009) for the preparation of spiked soil samples for the IAEA inter-comparison exercise on ^{137}Cs and ^{210}Pb activity measurements. A know mass of radioactive solution was put in the final containers and diluted with 80 mL of methanol. Then the soil powder was added and the methanol was totally absorbed by the powder. Samples were then dried and sealed. Similar procedure, but using acetone, was used by En-Chi Peng and Jeng-Jong Wang (2013).

The second approach is to spike larger quantities and then distribute them to smaller containers. It is usually achieved by spiking at a higher level than the final concentration a smaller quantity of the matrix used and then diluting it with the rest of material until homogenous distribution of radionuclides is obtained. This second approach was used by J. de Sanoit and R. Alvarez (1992) for the preparation of zeolite molecular sieves which were intended for use as environmental calibration standards. One molecular sieve consisting of A4 zeolite was spiked using a chromatographic method which uses the sorption properties of the zeolite and mixed with the non-spiked one. Two years later J. de Sanoit used another procedure for spiking, based on a rotary evaporator. A silica matrix was spiked with radioactive solution in presence of acetone. The acetone was consequently evaporated with a rotary evaporator. The spiked silica was mixed in a Turbula mixer with a blank matrix (1994). The method using rotary evaporator was later on used by V. Lourenço et al. for spiking grass samples. In this study separate batches were spiked in a sequence and at the end recombined and manually mixed (2014). The same principle – mixing a small batch of active matrix with a larger, non-active one – was used by S.M. Jerome to spike milk. However in this study instead of a rotary evaporator a laboratory spray-drier was used to produce milk powder containing desired levels of radioactivity and a planetary screw type mixer was used to mix the contaminated solution with the blank material (1993).

1.1.2 Feed matrix

A detailed literature study on the most popular kinds of animal feed was conducted. As a result of this study powdered maize grains were selected as a test material for the validation study.

Maize is, next to soybeans and wheat, among the three top feeding stuff products worldwide according to the FAO Statistical Database (FAO, 2002). Maize and wheat account for about half of all feed ingredients. They are both playing a major role as an efficient source of energy for the most popular species of farm animals like swine, milk and beef cattle and different kinds of poultry. Maize is also rich in highly digestible carbohydrates and relatively low in fibre, which is particularly important for swine and poultry. The level of proteins is however relatively low (9 to 11%), and for this reason supplementation with protein-rich feeds and amino acids is required (Ensminger, J.E., & Heinemann, 1990).

Maize as feedstuff can be used in the form of processed whole grains, a by-product of the milling industry (in the form of gluten meal, gluten feed and germ meal) and the whole plant silage (Newcomb, 1995). The maize grains are often processed prior to usage in order to facilitate the digestion. They can be fed to animals as a whole grain, ground, cracked, pelleted or steam flaked (OECD, 2002).

Furthermore, as homogenisation is part of a procedure of samples preparation for gamma spectrometric measurements, this material can be considered as representative also for other types of powdered grains.

2 Matrix material

2.1 Rice powder

Rice powder was used in the first tests of the spiking procedure as it was a material readily available from the Reference Materials Unit of the JRC Directorate F. The raw material consisting of 24 kg of rice grains originating from the USA and imported by Matthew's Foods, Glasgow, UK. It was bought from a regular food market in the UK. The grains were processed into fine powder. The procedure consisted of vacuum drying in a freeze-dryer (model Epsilon 2-85D Martin Christ, Osterode, Germany), cryogenic milling in a Palla vibrating mill (VM-KT, KHD Humboldt Wedag, Köln, Germany), sieving through a 125 µm stainless steel sieve (Russel Finex, London, Unigted Kingdom) and mixing using a 3-dimensional mixer (Dynamix CM-200 WAB, Basel, Switzerland). The water content was determined to be (8.2 ± 0.5) % (mass of water per mass of total material, k=1). Only a small quantity of this powder was available since it was produced for a different project.

2.2 Maize powder

Since the available amount of rice powder was limited, further testing was conducted using maize powder. The raw material consisting of 75 kg of maize grains was purchased from a commercial supplier in Belgium. The grains were processed into powder by Reference Materials Unit of the JRC Directorate F. The maize grains were placed in metallic drums and cooled down in liquid nitrogen for one night. Once cold, they were milled using a vibrating cryogenic mill (KHD Humboldt Wedag, Köln, Germany). A total amount of 64.7 kg of powder was collected. The powder was sieved over a 250 µm stainless steel mesh (Russel Finex Industrial sieve Model 17300, London, United Kingdom) connected to an ultrasonication probe (Russel Finex Vibrasonic 2000, London, United Kingdom) at room temperature. The fine fraction represented 57.1 kg and the coarse fraction 7.15 kg. The coarse fraction was re-milled and re-sieved as previously described. The fine fraction of the re-milled coarse fraction (amount 7.13 kg) was added to the 57.1 kg of the fine fraction obtained from the first milling/sieving sequence to give a total of 64.3 kg. The fine fraction was then placed in a 200 L metallic drum. It was mixed for two hours with a DynaMIX-CM200 mixer (WAB, Basel, Switzerland). The mixed powder was then split in 7 different plastic drums with ca. 10 kg each. The material was stored at +4 °C awaiting further use. Some samples were taken to be analysed with laser diffraction for the particle size distribution. The results of the tests are presented in Annex 1. The water content was determined to be (10.4 ± 0.5) % (mass of water per mass of total material, k=1).

3 Testing of rotary evaporator system

Between 17 and 24 of June 2014 testing of rotary evaporator provided by BÜCHI Labortechnik (Germany) was conducted. Samples of rice powder were used for these tests. 135 g of rice powder was placed in the flask of the rotary evaporator and then an adequate amount of liquid (ethanol, water, or acetone) was added. The amount of liquid necessary to adequately moisten the powder was determined experimentally. Four tests were conducted and different conditions were assessed. The parameters chosen for the tests were cooling, vacuum, rotations, position of the powder flask, and powder flask bath temperature. During all tests it was observed that already from the very beginning of the process of mixing and drying some of the material adhered closely to the walls of the flask and even when the whole content is completely dry it was hard to remove it from the flask. It was also noticed that if the vacuum is not applied the evaporation of the liquid was almost negligible despite increasing the temperature of the flask powder bath. The type of liquid used did not have a significant influence on the mixing and drying process.

The most satisfactory results were achieved while using acetone (BP 56.2 °C), bath temperature around 50 °C, vacuum (700 mbar) and cooling. These conditions enhanced the fastest evaporation of the liquid was and reduced the adhesion of powder on the walls of the flask.

4 Bulk material spiking and homogeneity testing

The quality of spiked reference materials depends to a large extent on the proper initial characterisation (Shakhashiro, Gondin da Fonseca Azeredo, Sansone, & Fajgelj, 2007). In order to characterise the massic activity of ^{137}Cs in the starting powder, three 30-g samples were each measured for 48 hours by γ-ray spectrometry, using a 36% relative efficiency coaxial HPGe detector (Canberra Industries, USA). It was found that the masic activity is below the detection limit (<1.6 Bq kg^{-1}) which was calculated on the basis of Currie's derivation (Currie, 1968) for the conditions of the given γ-ray measurements. All uncertainties in this chapter are provided as combined standard uncertainties with coverage factor k=1.

4.1 Spiking procedure

For the bulk spiking test, a known mass of the matrix substance was placed in the evaporation flask and mixed with appropriate amount of ethanol (BP 78.3°C) assuring the formation of a slurry and complete coverage of powder by the liquid. Then weighed portion of the radioactive solution containing ^{137}Cs was added. A rotary evaporator Hei-VAP with external cooling system purchased from company Heidolph (Germany) was used to perform the tests.

A standard solution of ^{137}Cs used was purchased from Physikalisch-Technische Bundesanstalt (PTB) and standardized at JRC Geel. A dilution of that solution with activity concentration of (276 ± 3) Bq·g^{-1} was used in the spiking process. A gravimetrically-determined aliquot of (1.203805 ± 0.000020) g was added to the slurry formed by mixing 250 mL of ethanol with 300 g of rice powder. The total activity of ^{137}Cs added to the rice powder was (332 ± 4) Bq.

The slurry was mixed for six hours using in a rotary evaporator (Hei-VAP, Heidolph, Germany). Then vacuum was applied in order to evaporate the ethanol. The spiked rice powder was consequently dried overnight in an oven at 55 °C. The whole batch was then transferred to a 1000 mL polypropylene container (CURTEC, Holland), mixed in a Turbula mixer (model T2F, Glen Mills Inc., USA) for six hours and divided into 10 portions of 30 g. Each portion was then placed in a 125 mL polypropylene container (Nalgene, USA) and further mixed for about 30 minutes using the Turbula mixer.

4.2 Characterisation and homogeneity studies

A homogeneity study was performed using all ten 125 mL polypropylene containers as minimum number of samples tested required by ISO Guide 35:2006 (ISO, 2006) for such studies. Samples were labeled R1 to R10.

In order to assess both the within-group and the between-groups homogeneity the content of each container was divided into two subsamples of 15 g each and placed in 125 mL polypropylene containers (Nalgene, USA). Twenty subsamples were obtained. Each subsample was then compacted by tapping using a Dual Autotap machine (model DA-1, Quantachrome Instruments, USA). Subsamples were measured using high resolution HPGe detector (Canberra Industries, USA) of 20% relative efficiency coaxial detector. The detector was connected via the usual chain of analogue electronics to the ADC and then to the MCA. The samples selected randomly were placed directly on the top of the detector and measured for 8 hours each. As the homogeneity measurements were relative measurements, there was no need to determine the absolute counting efficiency of the detector. The results of those measurements are shown in Table 1.

Table 1. Results of the ^{137}Cs count rate (cps) from the measurements of the 10 samples of spiked rice powder for the homogeneity test. Each original sample was split into 2 subsamples of 15 g each. The associated combined relative uncertainties, u, include counting statistics (including background), sample weighing, and geometry repeatability, (k=1).

	Subsample 1		Subsample 2	
	cps	u (%)	cps	u (%)
R1	0.063	2.03	0.063	2.11
R2	0.065	2.05	0.063	2.10
R3	0.060	2.03	0.061	2.07
R4	0.062	2.04	0.061	2.08
R5	0.065	1.99	0.062	2.13
R6	0.062	2.06	0.062	2.08
R7	0.062	2.10	0.060	2.10
R8	0.066	2.05	0.063	2.07
R9	0.064	2.07	0.064	1.99
R10	0.063	2.01	0.061	2.02
Mean value	0.062 ± 0.002			
Standard deviation	0.0014			
Relative Standard Deviation (%)	2.3			

Source: JRC analysis

The homogeneity test was conducted using the one way analysis of variance (ANOVA) test (ISO, 1976). The count rate of the 20 measured samples together with their combined relative uncertainties used for the calculations are shown in Table 2 and plotted in

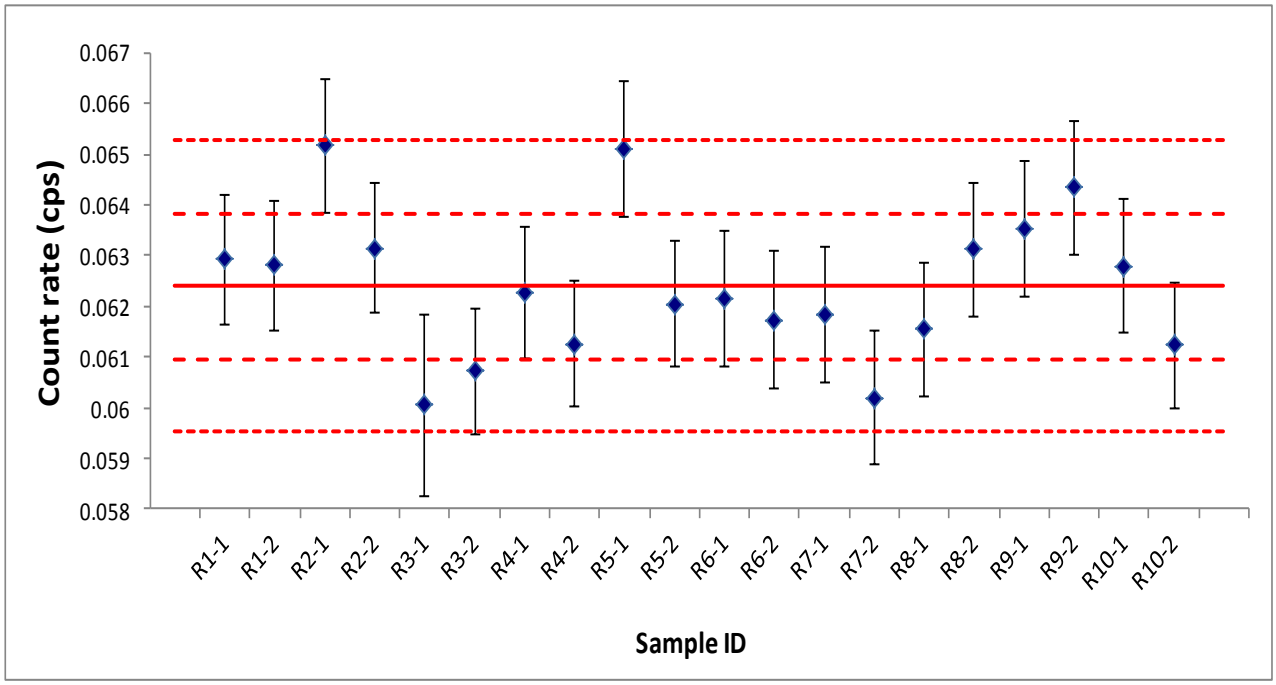
Figure **1**. The uncertainty budget consisted of counting statistics (including background), sample weighing, and geometry repeatability. The within-group variance and the between-groups variance were calculated and the results of those calculations are shown in Table 3. The Fisher distribution test (F-test) was performed and the results are also given in Table 3. The calculated F value is lower than the critical F value for one tailed test taken from the table of critical values for the F distribution at 95% level of confidence and the p value is higher than the α chosen (α = 0.05). Those results confirm that the within-group variance is not significantly higher than the between-groups variance and the material can safely be considered as homogeneous.

Table 2. ANOVA test parameters and results for the data in Table 2 (SS – sum of squares, MS – mean squares, d*f* – degrees of freedom, *F* – ratio of mean squares, p – probability, $F_{.05}$ – value taken from the table of critical values for the F distribution at 95% level of confidence).

Sources of variation	SS	MS	df	F	p	F .05
Between groups	$2.3 \cdot 10^{-7}$	$2.6 \cdot 10^{-8}$	9	0.0125	0.9910	3.0204
Within groups	$3.7 \cdot 10^{-5}$	$2.1 \cdot 10^{-6}$	10			

Source: JRC analysis

Figure 1. Count rate of 137Cs as measured in the 20 portions of spiked rice powder. Each original sample (R1 to R10) was split into 2 subsamples of 15 g each. Solid line represents the mean value and the coarse and fine dashed lines the (one and two) standard deviation(s) respectively of the results.



Source: JRC, 2016.

5 Testing of a method for individually spiked samples preparation

In order to prepare a validation study of a given method a reference material is required to determine the performance characteristics of the method. One of the characteristics is trueness defined as the closeness of agreement between a test result and the accepted reference value (ISO, 1994). The best situation is when a certified reference material is available, as it possesses a reference value. In this case however, as there are no available feed matrices contaminated with ^{131}I, ^{134}Cs and ^{137}Cs, maize powder samples were spiked with standard solutions of ^{131}I, ^{134}Cs and ^{137}Cs (Table 3).

Table 3. Information regarding the solutions used for spiking

Radionuclide	Solution supplier	Solution ID	Activity Bq·g^{-1}	Reference date
^{131}I	CMI (Czech Republic)	ER300915	228400±1%	23/10/2015 0:00 UTC
^{134}Cs	SCK•CEN (Belgium)	IRMM-AMP3-B1	6120±0.6%	1/1/2015 0:00 UTC
^{137}Cs	PTB (Germany)	AD1505	36622±0.85%	1/1/2015 0:00 UTC

Source: JRC analysis

5.1 Spiking procedure

In order to prevent the loss of activity samples were spiked directly into the container in which the measurement was carried out. Samples at three activity levels (low, medium and high) were prepared (~5, 1 and 0.2 Bq·g^{-1} per radionuclide). Samples on each levels are marked with an adequate sample code (e.g. VL1_1 - first sample on the high activity level, VL3_6 – sixth sample on the low activity level)

First, known amount of acetone was placed in the container (Nalgene, USA). The necessary amount was experimentally adjusted to assure that the whole amount of powder will be equally moist after it will be added to the container. Then known amounts of ^{131}I, ^{134}Cs and ^{137}Cs solutions were added in the container using a pycnometer (Canus Plastic Inc., Canada) with an elongated top. The amounts were determined gravimetrically using an analytical balance.

Containers were closed, placed on a laboratory shaker and mixed for 3 hours. Then, known amount of powder (~50 g) was added. Samples were dried overnight under the IR lamp and mixed for 3 hours in the Turbula mixer (model T2F, Glen Mills Inc., USA).

Samples were compacted by tapping 5.000 times on a Dual Autotap machine (model DA-1, Quantachrome Instruments, USA). The upper level was checked before the measurement was conducted and care was taken that it is horizontal. The height average of the upper level was measured and recorded.

5.2 Characterisation study

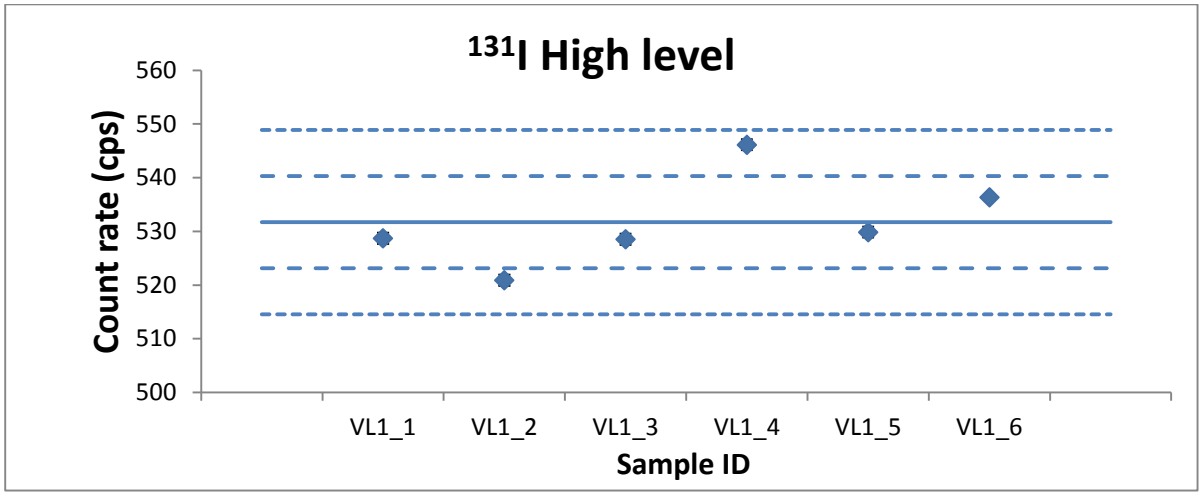
Samples were measured for 24, 16 and 8 h respectively using gamma-ray spectrometry. Results are plotted on Figures 2 to 13. Solid line represents the mean value; coarse and fine dashed lines represent value of one and two standard deviations (respectively).

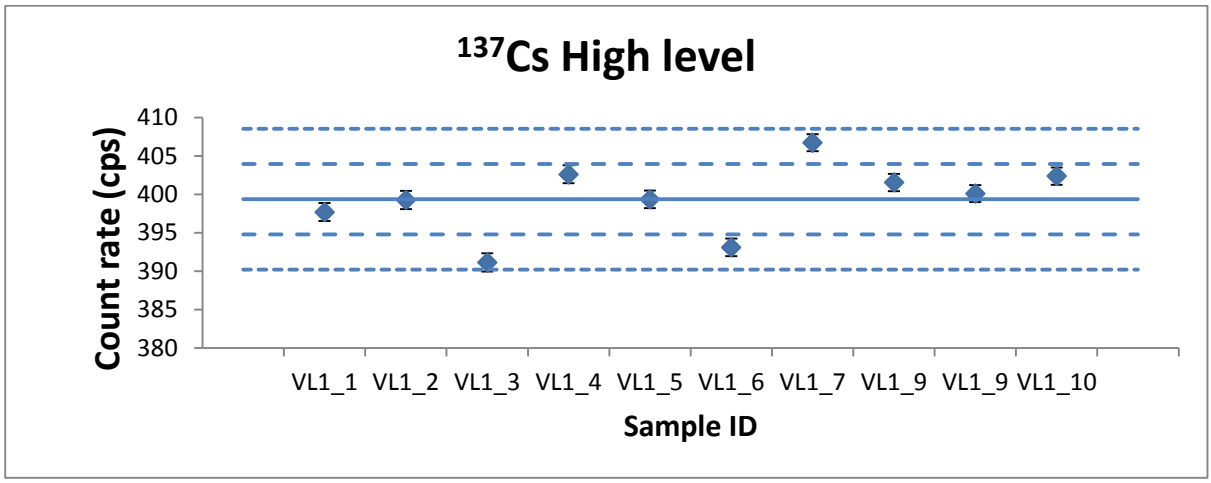
Samples were measured using a high resolution HPGe detector (Canberra Industries, USA), with 90% relative efficiency extended-range (XtRa) coaxial. The detector was connected via the usual chain of analogue electronics to the ADC and then to the MCA.

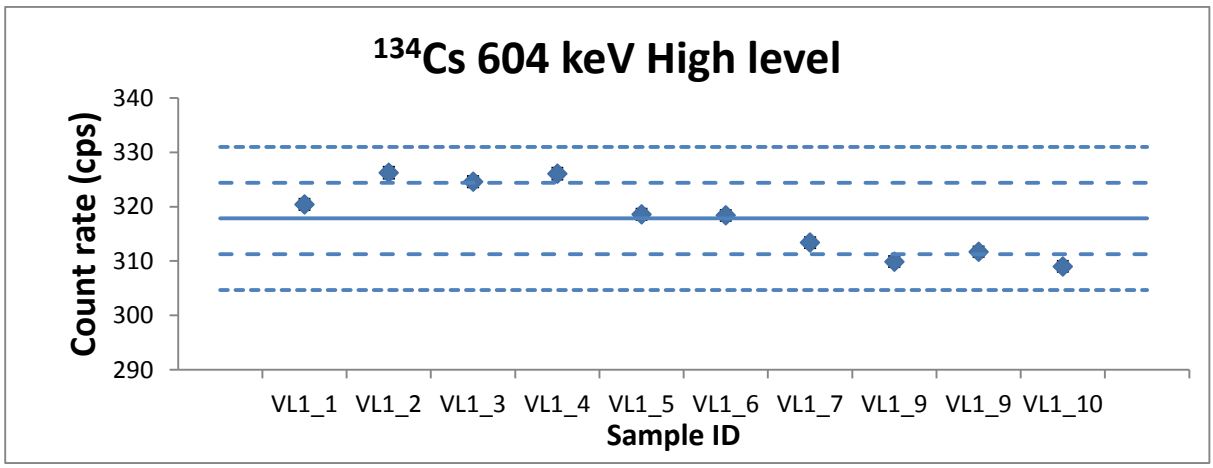
The data were corrected for decay since the reference date (23.11.2015), decay during the measurement and the background.

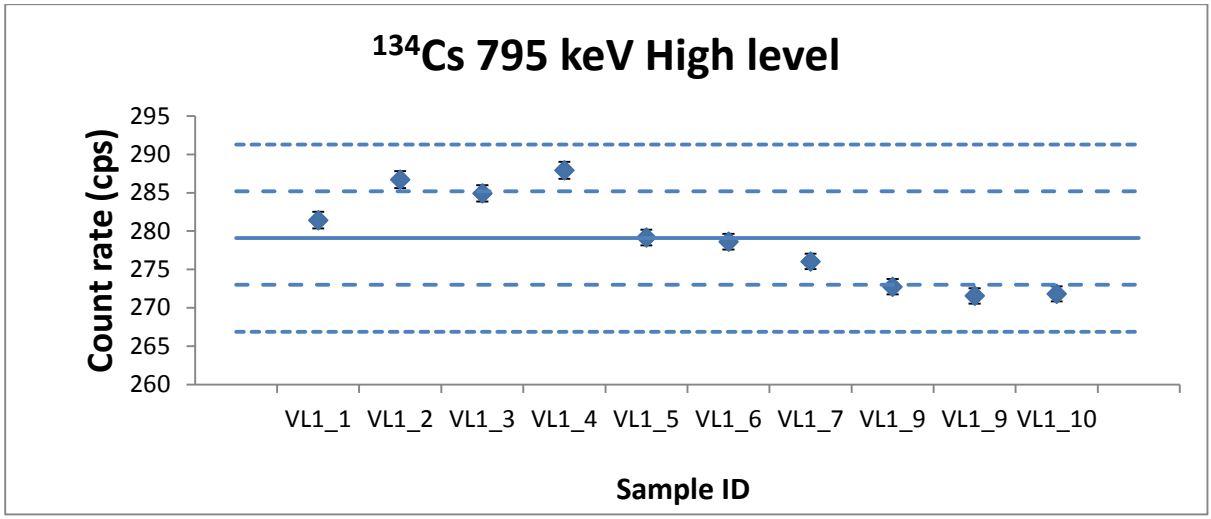
The uncertainty budget consisted of counting statistics (including background), sample weighing, half-life and geometry repeatability.

Figure 2. Count rate of ^{131}I, ^{137}Cs and two main gamma lines of ^{134}Cs at the high level of activity



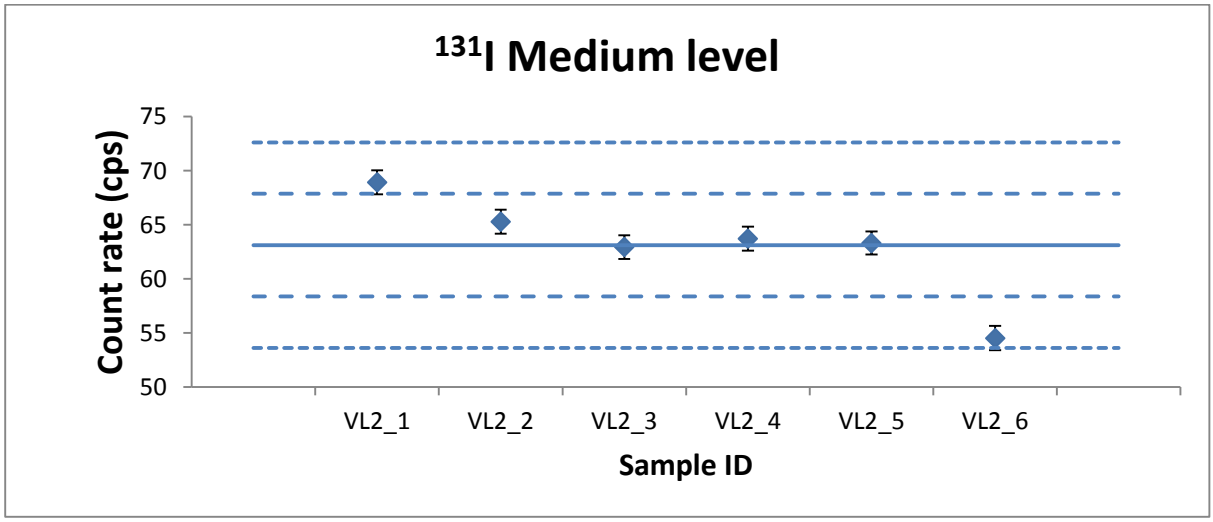


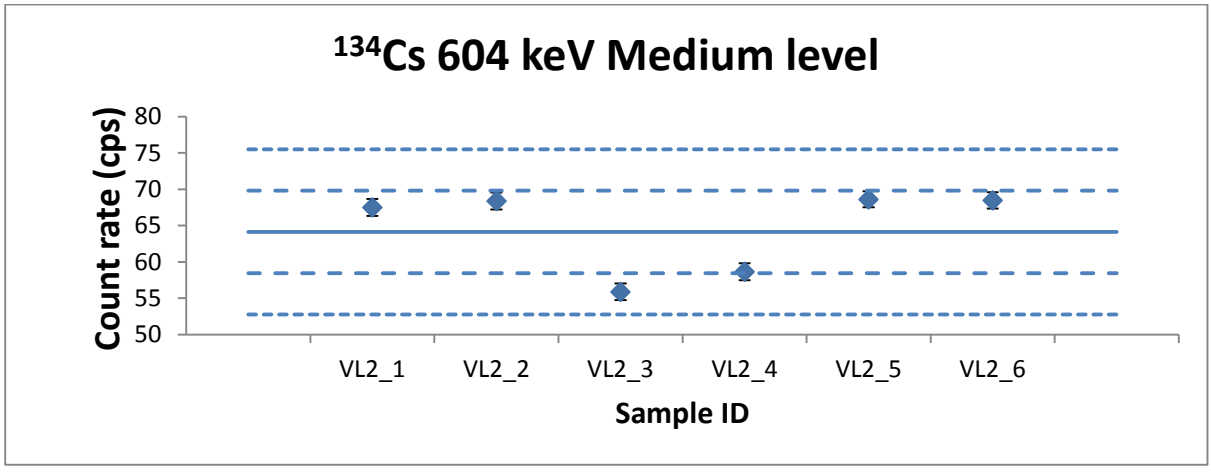


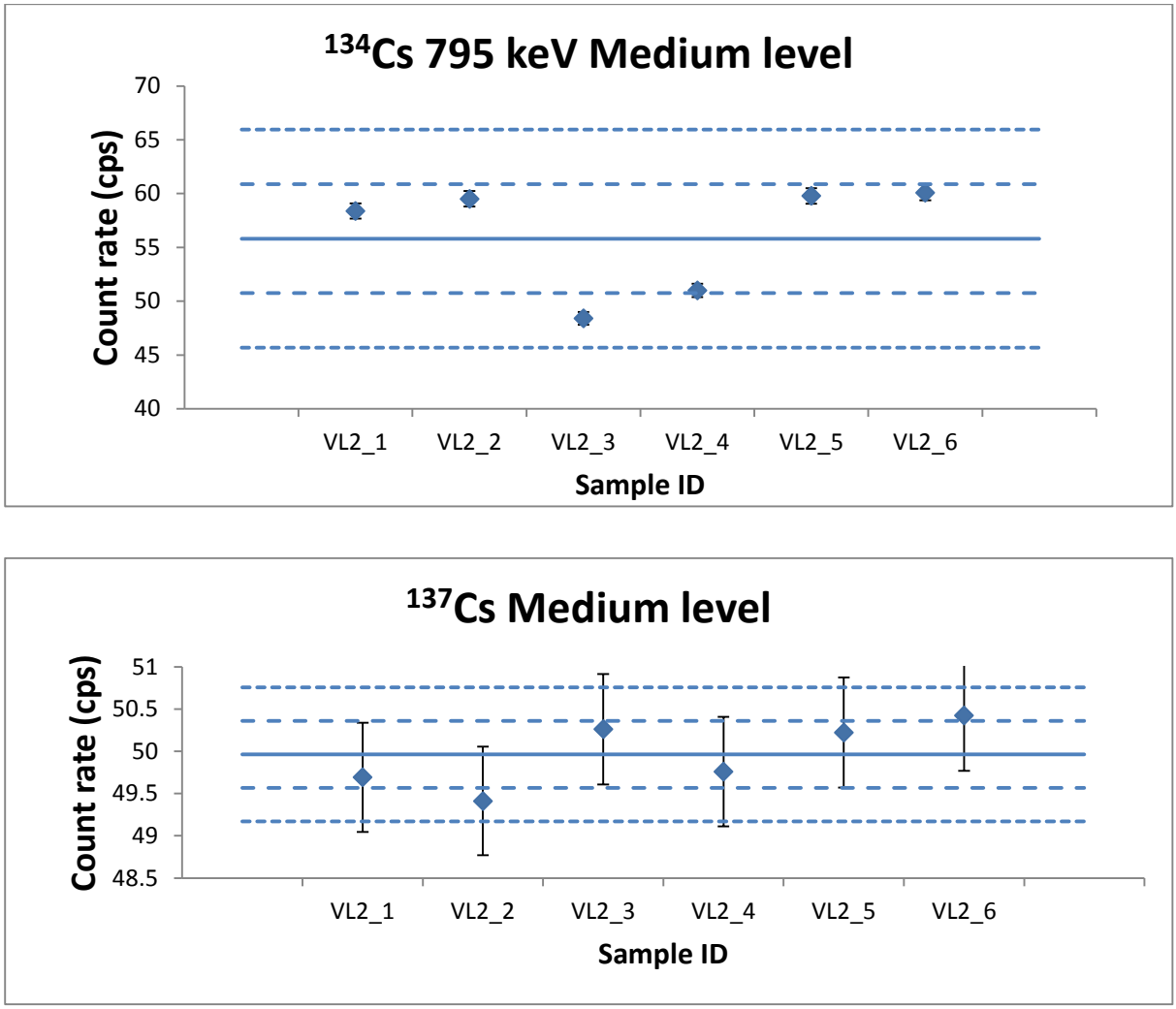


Source: JRC, 2016.

Figure 3. Count rate of ^{131}I, ^{137}Cs and two main gamma lines of ^{134}Cs at the medium level of activity

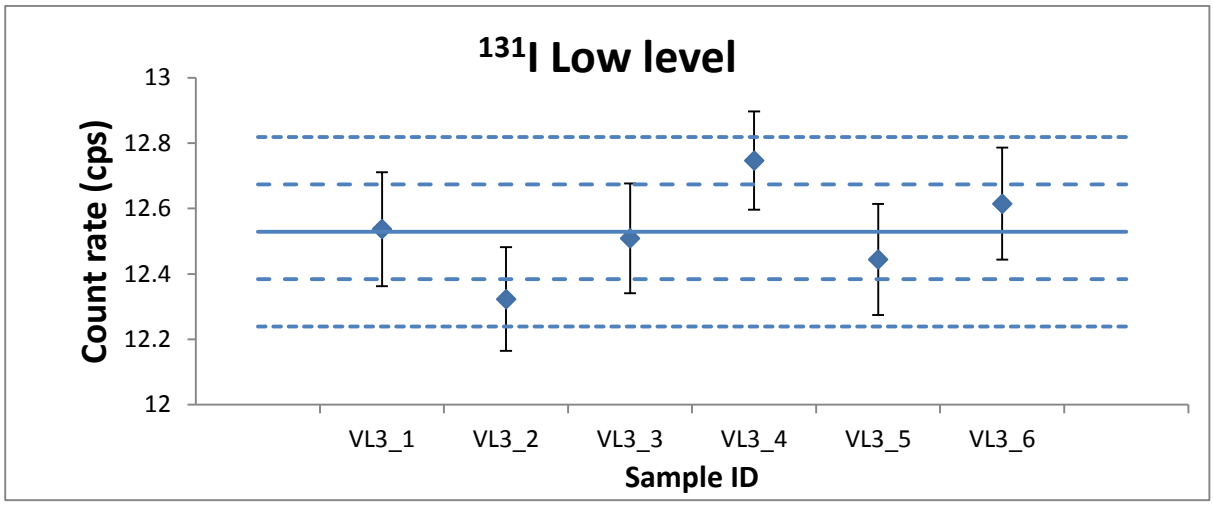


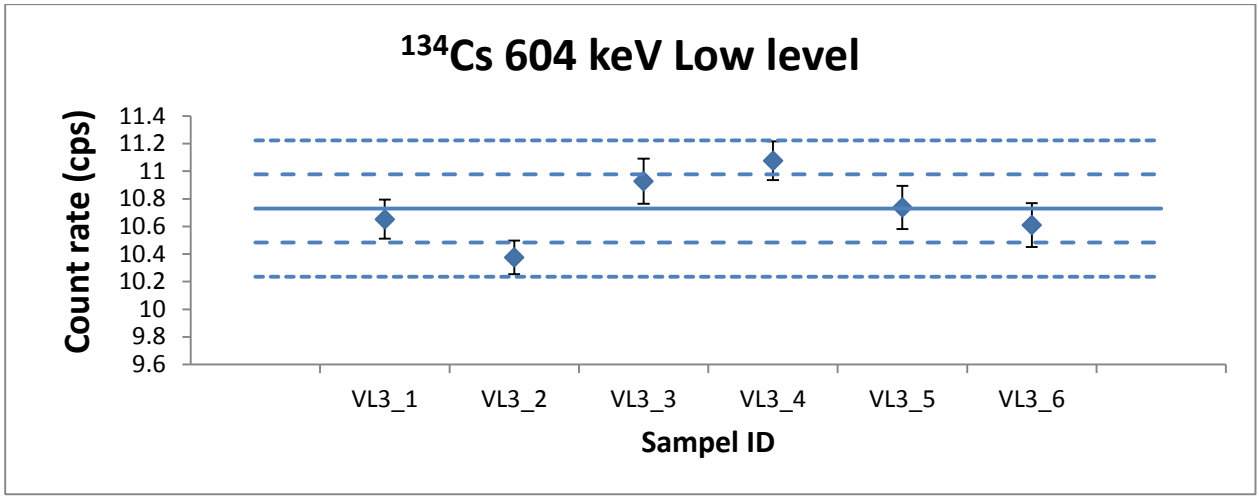


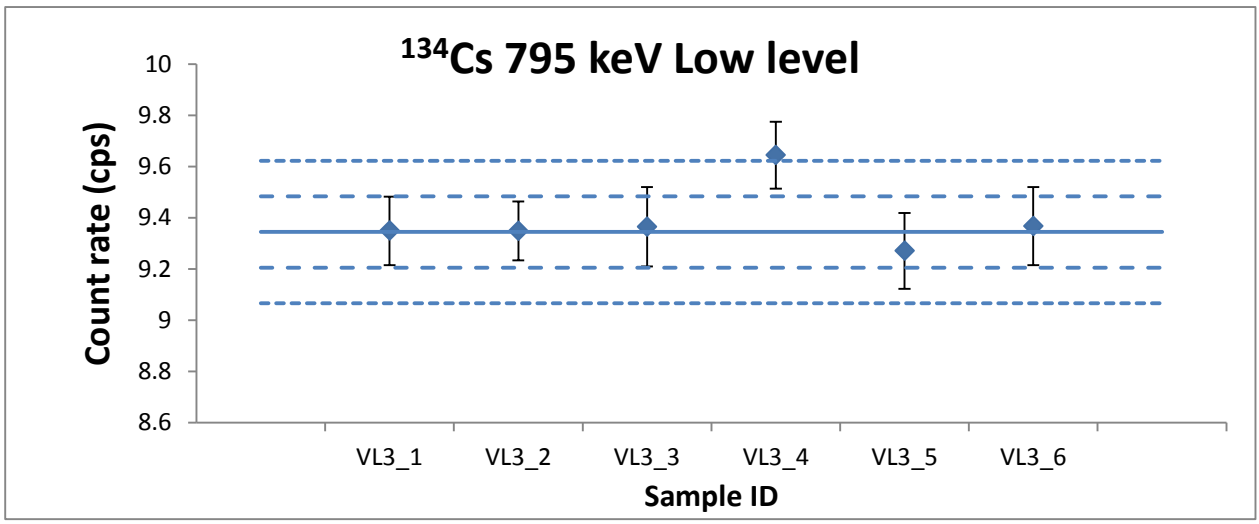


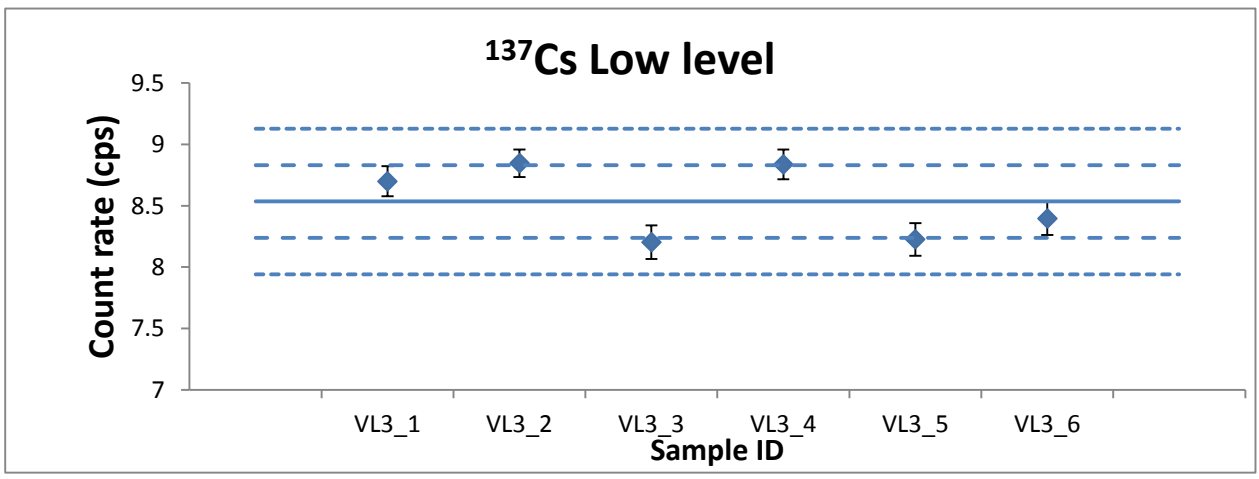
Source: JRC, 2016.

Figure 4. Count rate of ^{131}I, ^{137}Cs and two main gamma lines of ^{134}Cs at the low level of activity. The only identified outlier in the whole data set is highlighted in the graph for ^{134}Cs at energy 795 keV.









Source: JRC, 2016.

5.2.1 Calibration

The measurement method used for the gamma rays was high resolution gamma-ray spectrometry with High Purity Germanium (HPGe) detectors. This is an indirect method – a detection system is employed as a comparator of a sample to a reference source. Therefore the system must be calibrated.

A multi-nuclide solution purchased from Areva NP – LEA was used for calibration purposes. The certificate is enclosed in Annex 1.

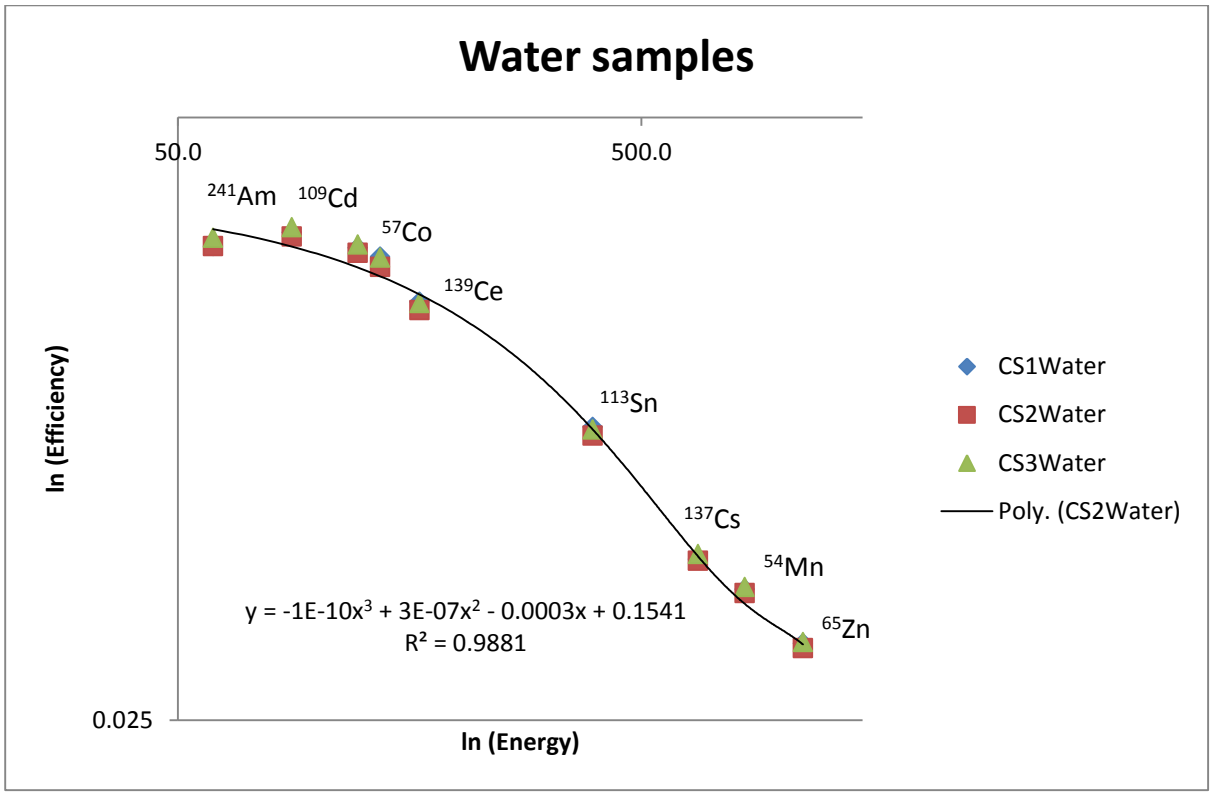
Energy calibration

Gravimetrically prepared multi-nuclide point sources were used to calibrate the detector in the current study.

Efficiency calibration

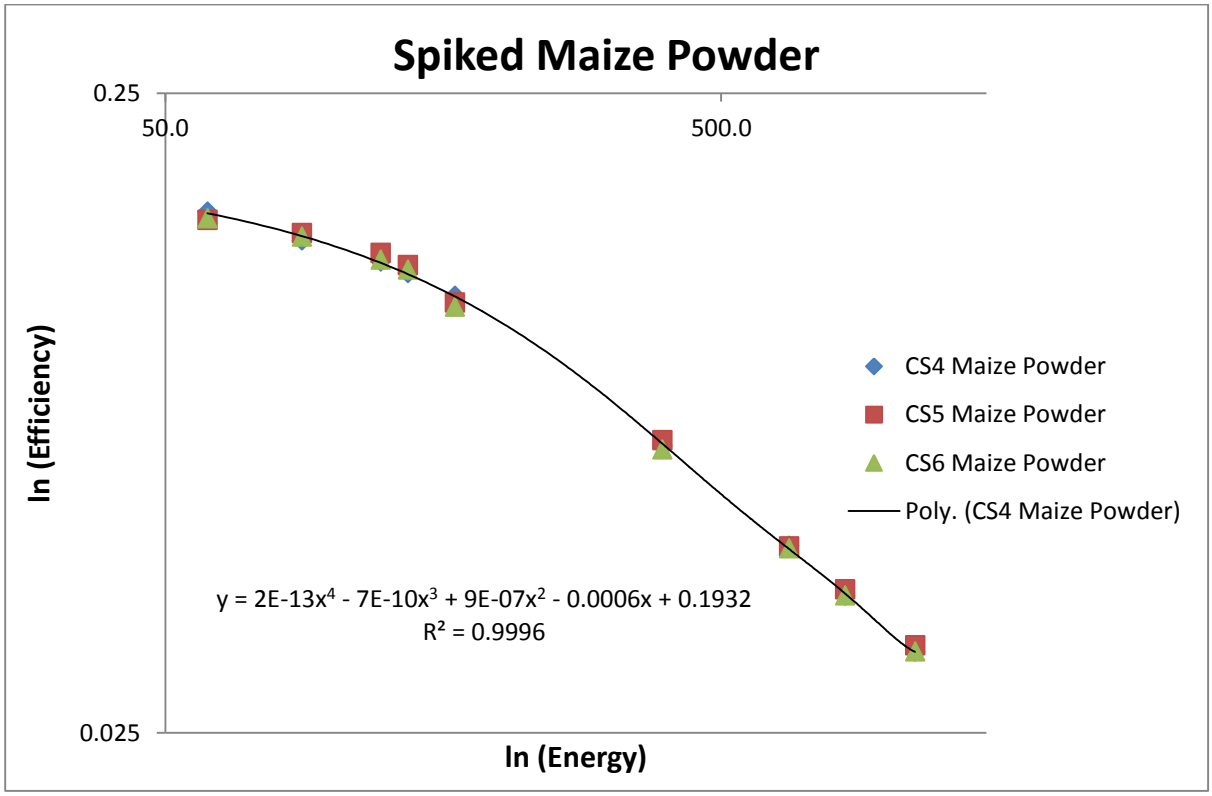
The preferred way of performing this calibration is to use a source of the same geometry and matrix as the one of the samples being measured. Therefore three sources consisting of maize powder were spiked with a multi-nuclide solution following the same procedure as the one used for the individually spiked samples. In addition, liquid sources were also prepared. The efficiency curves are displayed in **Figure 6**. The calibration curve used for calculations was the one for the sample CS5P.

Figure 5. Results of efficiency calculations for liquid samples spiked with the multi-nuclide solution



Source: JRC, 2016.

Figure 6. Results of efficiency calculations for maize powder samples spiked with the multi-nuclide solution



Source: JRC, 2016.

5.2.2. Results of activity calculations

On the basis of the conducted measurements the measured massic activity (a) of the samples was calculated on the basis of the following formula:

$$a = \frac{\mathrm{N}}{\varepsilon \cdot T_L \cdot m \cdot P_\gamma \cdot F}$$

where:

N is number of counts in the area of the full energy peak

ε is efficiency

T_L is live time in seconds

m is mass of the sample in grams

P_γ is γ-ray emission probability

F is the combination of the necessary correction factors (decay and FEP efficiency)

The results of activity calculations for the high level are presented in Table 4.

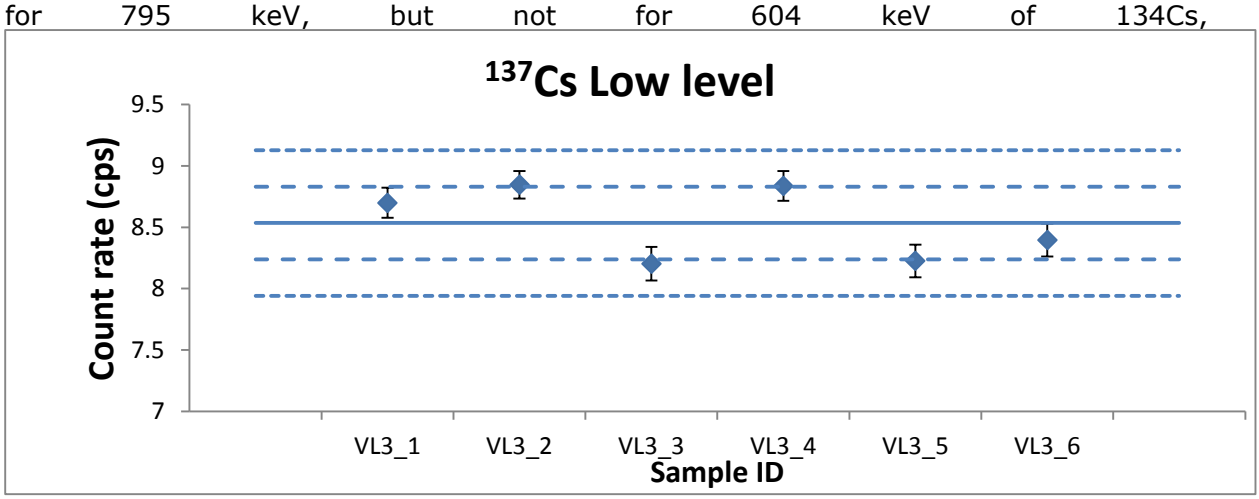
Table 4. Results of activity calculations at the high activity level for measured radionuclides. The expanded uncertainties are given (k=2)

Sample ID	A (Bq/g)												Deviation from the reference value (%)		
	measured						added								
	I-131	U %	Cs-134	U %	Cs-137	U %	I-131	U %	Cs-134	U %	Cs-137	U %	I-131	Cs-134	Cs-137
VL1_1	6.23	4.52	4.99	7.85	5.25	4.70	6.51	1	4.81	0.60	5.25	0.85	4.3	3.5	0.1
VL1_2	5.70	4.52	4.85	7.10	4.88	4.70	5.97	1	4.59	0.60	4.86	0.85	4.5	5.6	0.5
VL1_3	6.44	4.52	5.70	8.10	4.85	4.70	6.73	1	5.42	0.60	4.93	0.85	4.4	5.2	1.6
VL1_4	6.61	4.52	5.05	7.27	5.42	4.70	6.77	1	4.79	0.60	5.35	0.85	2.4	6.3	1.3
VL1_5	6.57	4.51	4.99	7.31	4.81	4.69	6.80	1	4.81	0.60	4.78	0.85	3.4	3.8	0.5
VL1_6	5.54	4.51	5.27	7.14	4.93	4.69	5.71	1	5.06	0.60	4.99	0.85	3.0	4.2	1.1
VL1_7	N/A	N/A	5.44	7.32	5.70	4.68	N/A	N/A	5.29	0.60	5.57	0.85	N/A	3.0	2.4
VL1_8	N/A	N/A	5.50	7.21	4.74	4.69	N/A	N/A	5.40	0.60	4.69	0.85	N/A	1.9	1.1
VL1_9	N/A	N/A	5.83	7.33	4.64	4.68	N/A	N/A	5.70	0.60	4.61	0.85	N/A	2.2	0.7
VL1_10	N/A	N/A	6.32	7.40	4.86	4.68	N/A	N/A	6.17	0.60	4.79	0.85	N/A	2.4	1.3
Mean	**6.18**	**4.52**	**5.39**	**7.40**	**5.01**	**4.69**	**6.42**	**1**	**5.20**	**0.6**	**4.98**	**0.85**	**3.7**	**3.8**	**1.1**
SD	**0.46**		**0.44**		**0.34**		**0.46**		**0.49**		**0.31**				

Source: JRC analysis

5.2.3 Grubbs test

The Grubbs test was applied in order to assess if there are any outlying results in the data sets (ISO, 1994). Only one sample was identified as an outlier (sample VL1_4 only for 795 keV, but not for 604 keV of 134Cs,



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5.2.4 Geometry reproducibility of measurements

Samples were placed on the detector endcap without a holder and were positioned by hand; therefore it was necessary to check the geometry reproducibility. In order to assess it one sample was repositioned in front of the detector each time and measured 5 times. The standard deviation was calculated to be 0.5% and was included in the uncertainty calculations.

6 Conclusions

Spiking tests were conducted of bulk and individual powder spiking with radioactive solution.

Firstly, a test material spiked with solution containing anthropogenic radionuclide ^{137}Cs was prepared following the requirements of ISO Guide 35 (ISO, 2006). A homogeneity study was performed, in order to assess all components of the uncertainty for the further full characterisation study of the reference material and this is crucial to assure adequate level of test material quality. According to the conducted measurements and calculations, the so-prepared reference material is homogeneous down to at least 15 g sample size. This result confirms the usefulness of the tested method for the preparation of spiked reference materials for proficiency testing of γ-ray measurements.

Secondly, three sets of individually spiked samples were prepared having different activity levels of the three radionuclides concerned. In this test the relative deviation between the amount of the activity added and the calculated massic activity values is low and lower than the values of uncertainty calculated for the measured activity values. Therefore it can be stated that the closeness of agreement between the activity added to the sample and activity measured is satisfactory. This proves that these samples may be used as a reference material.

On the basis of the conducted tests it can be stated that both methods of spiking are suitable for the future use in the method validation study and for the preparation of the proficiency testing exercise for EU MS monitoring laboratories.

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List of abbreviations and definitions

ADC	analog-to-digital converter
ANOVA	analysis of variance
BP	boiling point
CEN	European Committee for Standardization
cps	counts per second
df	degrees of freedom
F	ratio of mean squares
F.05	value taken from the table of critical values for the F distribution at 95% level of confidence
FAO	Food and Agriculture Organization of the United Nations
HPGe	high purity Germanium
IAEA	International Atomic Energy Agency
IR	infrared
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	coverage factor
mbar	millibar, one thousandth of a bar, the unit of atmospheric pressure equivalent to 100 pascals
MCA	multichannel analyser
MS	mean squares
p	probability
SS	sum of squares
T1/2	half-life

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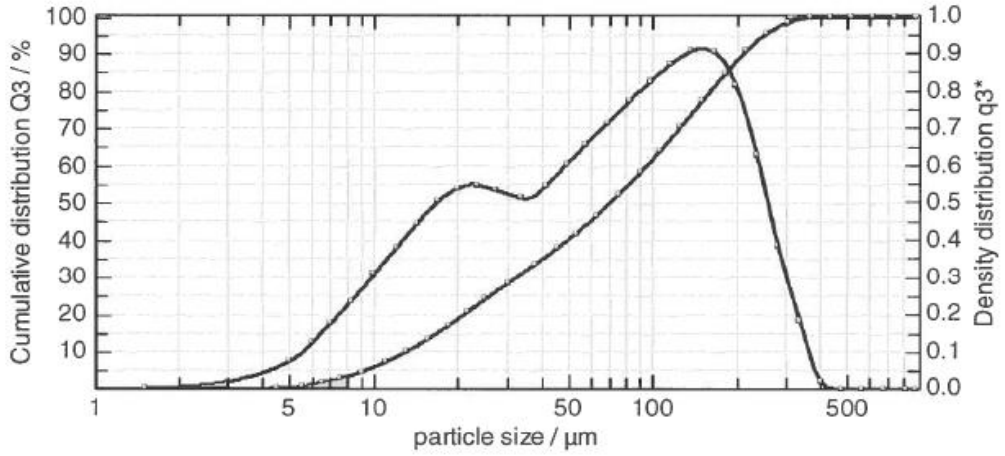
Annexes

Annex 1. Particle size analysis by laser light diffraction

Distribution of the equivalent sphere diameter based on the measurement of three samples.



Annex 2. Calibration certificate

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Type :

N° d'identification : **8020/5**
Identification number :

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1 Means and methods

Term characterized	Photon flux
Unit	$\gamma.s^{-1}$
Type of detector	Solid state detectors Ge-HP
Reference of the measurement equipment	CSGHP1/6
Method used	γ-ray spectrometer

The environmental conditions have not influence on the results of the measurement.

2 Nominal characteristics for the delivered standards

Reference	Multigamma reference : **12ML01ELMA60 - n° : 8020/5**
Type of container (*)	**A**
Classification	No sealed source
Volume	**1 cm^3**
Mass & Theoritical density	m=1.0231 g ; d=1.016 (***)
Chemical composition	Chloride of each component + $EuCl_3$ for ^{241}Am in HCl 1N
Reference date	**November 30th. 2015 at 12 h. UTC**
No surface contamination (**)	**Wipe test : OK September 21th. 2015**
Technician measures	**R.RIBES**

(*) See product characteristics in LEA catalogue (www.lea-cerca.com)
(**) According to NF M61-003 / ISO 9978
(***) Mass and density are not covered by Cofrac Accreditation.

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3 Results

3-1 Photonic flux

Standard multigamma type 12ML01ELMA60 reference 8020/5				
Racionuclide	Energy in keV(*)	Number of photons per 100 disintegrations (*)	Photon flux in s^{-1} g^{-1}	Extended relative uncertainty in (k=2)
^{241}Am	59.5409 ± 0.0001	35.92 ± 0.17	7.29E+03	± 4.0
^{109}Cd	88.0336 ± 0.0010	3.66 ± 0.05	7.21E+03	± 5.5
^{57}Co	122.06065 ±0.00012	85.51 ± 0.06	8.49E+03	± 3.0
^{57}Co	136.47356 ± 0.00029	10.71 ± 0.15	1.063E+03	± 3.0
^{139}Ce	165.857 ± 0.003	79.90 ± 0.04	1.048E+04	± 4.0
^{51}Cr	320.0835 ± 0.0004	9.89 ± 0.02	1.984E+04	± 4.5
^{113}Sn	391.698 ± 0.003	64.97 ± 0.17	2.426E+04	± 4.0
^{85}Sr	514.0048 ± 0.0022	98.5 ± 0.4	3.29E+04	± 3.5
^{137}Cs	661.657 ± 0.003	84.99 ± 0.2	4.25E+04	± 3.0
^{54}Mn	834.848 ± 0.003	99.9752 ± 0.0005	5.31E+04	± 3.0
^{88}Y	898.036 ± 0.004	93.90 ± 0.23	5.84E+04	± 3.0
^{65}Zn	1115.539 ± 0.002	50.22 ± 0.11	7.53E+04	± 3.0
^{60}Co	1173.228 ± 0.003	99.85 ± 0.03	7.47E+04	± 3.0
^{60}Co	1332.492 ± 0.004	99.9826 ± 0.0008	7.48E+04	± 3.0
^{88}Y	1836.052 ± 0.013	99.32 ± 0.03	6.18E+04	± 3.0

(*) Values recommanded by the LNHB (https://www.nucleide.org).

3-2 Concentration activity for each radionuclide

Radionuclide	Activity concentration kBq.g^{-1}	Extended relative uncertainty in % (k=2)
^{241}Am	20.30E+0	± 4.0
^{109}Cd	197E+0	± 5.5
^{57}Co	9.93E+0	± 3.0
^{139}Ce	13.12E+0	± 4.0
^{51}Cr	200.6E+0	± 4.5
^{113}Sn	37.3E+0	± 4.0
^{85}Sr	33.4E+0	± 3.5
^{137}Cs	50.0E+0	± 3.0
^{54}Mn	53.1E+0	± 3.0
^{65}Zn	151.9E+0	± 3.0
^{60}Co	74.8E+0	± 3.0
^{88}Y	62.2E+0	± 3.0

The extended uncertainties mentionec are those corresponding to two incertitude composed type. The uncertainties types have been calculated taking into account the different uncertainties components: reference standards, means if calibration, environmental conditions the data of the calibrated instrument, repeatability...

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